

## THE TEMPERATURE DEPENDENCE OF ELECTRICAL CONDUCTIVITY

BY WILLIAM V. HOUSTON  
CALIFORNIA INSTITUTE OF TECHNOLOGY

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## ABSTRACT

To explain the fact that the resistance of a pure metal becomes zero at the absolute zero of temperature it is necessary to take into account the restrictions placed upon the electron scattering by the quantum statistics. When these are included as a probability of transition, the Brillouin treatment of wave scattering gives a very satisfactory law of the temperature dependence of resistance.

IN A previous paper it was shown that electrical resistance is caused by the diffraction of the electron waves.<sup>1</sup> The waves of the electrons which contribute essentially to the conductivity are so long that if the ions of the crystal were regularly arranged and stationary, they would pass freely through the lattice without retardation. The irregular motion due to temperature energy, however, causes a general scattering in all directions. This general scattering produces a resistance which increases with the temperature. For the computation of this increase, the work of Debye on the scattering of x-rays provided a convenient method.<sup>2</sup> This served admirably to show the validity of the fundamental idea, but it is not quite correct at very low temperatures. Frenkel and Mirolubow<sup>3</sup> have avoided this difficulty by using the work of Brillouin<sup>4</sup> on the scattering of light, and they find that the resistance should increase with the third power of the temperature for very low temperatures. In their work, however, the mean free path is not introduced in quite the same way as in the work of Sommerfeld, who followed Lorentz.<sup>5</sup> A treatment by the method of Lorentz gives a slightly different law of variation with temperature.

When account is taken of the fact that an isolated ion does not scatter uniformly in all directions, the properties of the ion are found to affect the temperature coefficient of conductivity as well as the value of the conductivity itself. This is in accord with the experiments which have shown that no single function can represent exactly the temperature dependence of the conductivity for all metals.

However, all of these treatments are based upon the idea that the resistance of a metal is due wholly to the temperature motion of the ions in the crystal lattice. Hence, if the resistance becomes zero at the absolute zero

<sup>1</sup> W. V. Houston, *Zeits. f. Physik* **48**, 449 (1928).

<sup>2</sup> P. Debye, *Ann. d. Physik* **43**, 49 (1914).

<sup>3</sup> Frenkel and Mirolubow, *Zeits. f. Physik* **49**, 885 (1928).

<sup>4</sup> Brillouin, *Ann. de Physique* **17**, 88 (1922).

<sup>5</sup> H. A. Lorentz, *Theory of Electrons*; A. Sommerfeld, *Zeits. f. Physik* **47**, 1 (1928).

of temperature, it must be assumed that the temperature motion of the ions also becomes zero at this point. But it is almost certain that this is not the case. On the one hand, the quantum theory in its present form indicates that a harmonic oscillator in its lowest state possesses a half unit of energy, i.e.  $E_0 = \frac{1}{2}h\nu$  and therefore, presumably a considerable amount of motion. (If every standing wave which can exist in a crystal is present with  $\frac{1}{2}h\nu$  of energy, the ions must be far from a state of rest.) On the other hand, the experiments which have been made to determine the intensity of the x-ray diffraction pattern as a function of the temperature seem to point rather clearly to the existence of zero point energy and a zero point motion of the system.<sup>6</sup>

The solution of this difficulty also is to be found in the work of Brillouin, when it is combined with the Fermi statistics. According to Brillouin, the light reflected from an elastic wave has a frequency equal to the sum or the difference of the frequencies of the incident light wave and the elastic wave. Since the frequency of an electron wave is proportional to its energy, it is evident that this means that the electron impacts are all inelastic, and that the electron either loses or gains an energy equal to  $h\nu$  where  $\nu$  is the frequency of the elastic wave.<sup>7</sup> But the electron can gain energy only when two conditions are fulfilled. First, there must be a vacant state of higher energy to which the electron can jump; and second, the elastic wave must be able to lose the energy which the electron gains. This means that the elastic wave cannot be in its lowest energy state before the impact. On the other hand, the electron can lose energy only when there is a vacant state of lower energy to which it can jump. In this case, the state of the elastic vibration is not important since the elastic oscillator can always absorb energy.

It is not difficult to derive an expression for these restrictions. Sommerfeld has shown that only electrons whose velocities are close to the critical velocity  $\bar{v}$  need be considered in computing the conductivity.  $\bar{v}$  is given by  $m\bar{v}^2/2kt = \log A$ , where  $A$  is the constant in the distribution function of the Fermi statistics. After an impact these electrons will have the energy  $(\frac{1}{2})m\bar{v}^2 \pm h\nu$ . Thus the probability that there is a place of higher energy to which the electron can jump is

$$P' = 1 - 1/\left\{ (1/A)e^{[(m\bar{v}^2/2) + h\nu]/kT} + 1 \right\} = 1/(1 + e^{-h\nu/kT}). \quad (1)$$

But at the same time the elastic vibration must be able to lose energy. The probability that an oscillator is not in its state of lowest energy, i.e. that  $E = (n + 1/2)h\nu$  where  $n > 0$  is

$$P'' = e^{-h\nu/kT}. \quad (2)$$

For these two conditions to be satisfied at the same time, there is the probability

<sup>6</sup> James, Waller and Hartree, Roy. Soc. Proc. **A118**, 334 (1928).

<sup>7</sup> This fact and its consequences were first recognized by Bloch, Zeits. f. Physik **52**, 555 (1928). However, he did not explicitly develop the law of temperature dependence which results from it in the simple way given here.

$$P_1 = P'P'' = 1/(e^{h\nu/kT} + 1). \quad (3)$$

The probability that the electron can lose energy is given by

$$P_2 = 1 - 1/\{(1/A)e^{[(m\bar{v}^2/2) - h\nu]/kT} + 1\} = 1/(e^{h\nu/kT} + 1) \quad (4)$$

Then the probability that one or the other of these processes can take place is merely half the sum of the two probabilities

$$P = (1/2)(P_1 + P_2) = 1/(e^{h\nu/kT} + 1). \quad (5)$$

For  $T = 0$ ,  $P = 0$ , so that no scattering can take place regardless of the motion of the crystal lattice.

We may now briefly outline the application of this restriction to the computation of the electrical resistance. Frenkel and Mirolubow have given a concise presentation of the theory of Brillouin so we may use the equations as given by them. When account is taken of the zero point energy, the intensity per unit solid angle scattered in a given direction is given by

$$S = S_1 n^2 w h Q \kappa V \{1/(e^{hwQ/kT} - 1) + \frac{1}{2}\} \quad (6)$$

$V$  is the volume of the crystal which does the scattering, and  $Q$  is the reciprocal of the wave-length of the elastic wave which does the scattering.  $Q$  satisfies the relation

$$Q = 2q \sin(\theta/2) \quad (7)$$

where  $q$  is the reciprocal of the wave-length of the incident electron wave and  $\theta$  is the angle of scattering.  $w$  is the velocity of the elastic wave in the crystal,  $n$  is the number of atoms per unit volume, and  $\kappa$  is the compressibility.  $S_1$  is the intensity scattered by a single atom in the given direction. Frenkel and Mirolubow treat this as independent of the direction.

As usual, we write the expression for the distribution function when a current is flowing in the  $x$  direction, as

$$f(\xi, \eta, \zeta) = f_0(\xi, \eta, \zeta) + \xi \chi(v) \quad (8)$$

where  $\xi$ ,  $\eta$ ,  $\zeta$  are the velocity components and  $f_0$  is the function when no current is flowing. The expression for  $\chi(v)$  then is

$$\begin{aligned} -8\chi n^2 w h \kappa V \int S_1 \{1/(e^{hwQ/kT} - 1) + \frac{1}{2}\} \{1/(e^{hwQ/kT} + 1)\} (\xi' - \xi) Q \sin \theta d\theta d\phi \\ = \frac{eF}{m} \frac{\partial f}{\partial \xi} + \xi \frac{\partial f}{\partial x}. \end{aligned} \quad (9)$$

In Eq. (9),  $\nu$  is replaced by  $wQ$ , and  $\xi'$  is the  $x$  component of the velocity to which the electron is scattered by the impact. In this equation the small change of total velocity, due to the exchange of energy, may be neglected.  $\xi'$  can then be expressed terms of  $\xi$ ,  $\theta$ ,  $\phi$ . If the integration is carried out with respect to  $\phi$  and the result is expressed in terms of  $\theta/2$ , we may use Eq. (7) to express the integral as follows:

<sup>8</sup> Reference 1, Eq. (6).

$$\frac{8\pi\chi n^2 w h\kappa V}{q^4} \int S_1 \left\{ \frac{1}{(e^{2hwQ/kT}-1)} + \frac{1}{2(e^{hwQ/kT}+1)} \right\} Q^4 dQ = \frac{eF}{m} \frac{1}{\xi} \frac{\partial f}{\partial \xi} + \frac{\partial f}{\partial x} \quad (10)$$

If we now assume that  $S_1$  has the form given by Wentzel<sup>9</sup> and again use Eq. (7) and simplify, we have:

$$\frac{2\pi\chi Z^2 e^4 n^2 w h\kappa}{m^2 v^3} \int \frac{Q^4 dQ}{(e^{hwQ/kT}-1)(Q^2+4q^2c)^2} = \frac{eF}{m} \frac{1}{v} \frac{\partial f}{\partial v} + \frac{\partial f}{\partial x}. \quad (11)$$

In this equation,  $c = \lambda^2/16\pi^2 b^2$ , where  $b$  is a measure of the extent of the ion, and  $q^2 = 1/\lambda^2$ , so that  $4q^2c = 1/4\pi^2 b^2 = aQ_1^2$ . If we let  $hwQ/kT = x$ , and  $hwQ_1/k = x_0$ , we may write for the reciprocal mean free path, which is proportional to the resistance:

$$l^{-1} = \frac{2\pi Z^2 e^4 n^2 \kappa \Theta k}{m^2 v^4} \frac{1}{x_0} \int_0^{x_0} \frac{x^4 dx}{(e^x - 1)(x^2 + ax_0^2)^2}. \quad (12)$$

The upper limit of this integration, at least for monovalent metals, may be taken as  $\Theta/T$  where  $\Theta$  is the characteristic temperature of Debye. For metals where the wave-length of the electrons considered is less than twice the minimum wave-length of the elastic vibrations, the upper limit may have to be modified. However, the limit is always uncertain since the shortest elastic vibrations are certainly not sinusoidal.

Eq. (12) shows that the resistance should become zero with the temperature even when the zero point energy is considered. This is due entirely to the restriction imposed by Pauli's principle and the fact that all scattering is with change of wave-length. This restriction is expressed by  $P$  in Eq. (5). Above the zero point, the rate of change of resistance depends upon the factor  $a$ . When  $a$  is large, that is, when the scattering of a single ion is the same in all directions, the resistance should increase with the fifth power of the temperature for very low temperatures, and with the first power of the temperature for temperatures large compared with  $\theta$ . When  $a$  is very small, the resistance is proportional to  $T$  for low temperatures. The observed variation lies, of course, somewhere between these limits.

The integral in Eq. (12) can be expanded for values of  $x_0$  which are not too large, and then integrated. The result is:

$$\frac{1}{x_0} \int_0^{x_0} \frac{x^4 dx}{(e^x - 1)(x^2 + ax_0^2)^2} = \frac{A}{x_0} - \frac{B}{2} + \frac{Cx_0}{12} - \frac{Dx_0^2}{720} + \dots \quad (13)$$

where

$$\begin{aligned} A &= \frac{1}{2} \left\{ \log(a+1)/a - 1/(a+1) \right\} \\ B &= \left\{ (3a+2)/2(a+1) - (3a)^{1/2}/2 \right\} \tan^{-1}(1/a^{1/2}) \\ C &= \frac{1}{2} \left\{ (2a+1)/(a+1) - 2a \log(a+1)/a \right\} \\ D &= \frac{1}{2} \left\{ (a+1)^2/2 - 3a(a+1) + 3a^2/2 + a^3/(a+1) + 3a^2 \log(a+1)/a \right\} \end{aligned} \quad (14)$$

<sup>9</sup> G. Wentzel, *Zeits. f. Physik* **40**, 590 (1926); Reference 1, Eq. (14).

The resistance can be found by inserting the value of  $l$  in Sommerfeld's equation. This gives for the resistance of gold  $1.45 \times 10^{-18}$  if  $a$  is taken as 0.1. The observed value is  $2.28 \times 10^{-18}$ . With this value of  $a$ , the resistance as a function of temperature is given in Table I. The values of  $R/R_0$  for high temperatures are determined from Eq. (13), and for low temperatures by a rough graphical integration. The agreement with the observed values could be improved by adjusting the constant  $a$ .

TABLE I.  $R/R_0$  for gold with  $a=0.1$  and  $\theta=190$ .

$T$	20.4	68	90	169	273	573	773
$R/R_0$ cal.	0.007	0.15	0.23	0.56	1.00	2.34	3.25
$R/R_0$ obs.	0.006	0.177	0.270	0.592	1.00	2.24	3.16

We may, also, write the expression for the variation of resistance with pressure in a simple form. The resistance itself may be written:

$$R = E\kappa f(\Theta/T) \quad (15)$$

where  $E$  is independent of the pressure. We then have the expression:

$$\frac{1}{R} \frac{dR}{dp} = \frac{1}{\kappa} \frac{d\kappa}{dp} - \frac{T}{f\Theta} \frac{df}{dT} \frac{d\Theta}{dp}. \quad (16)$$

Since

$$\Theta = \text{const}/\rho^{1/6} \kappa^{1/2}$$

this may be written

$$\frac{1}{R} \frac{dR}{dp} = \left(1 + \frac{2T}{f} \frac{df}{dT}\right) \frac{1}{\kappa} \frac{d\kappa}{dp} + \frac{\kappa T}{6\rho f} \frac{df}{dT}. \quad (17)$$

This gives the correct order of magnitude for the effect.

We may then conclude that the restriction of the transition probabilities on account of the degeneration of the electron gas, not only explains why the resistance goes to zero at the absolute zero, but when combined with the scattering equations of Brillouin, gives a very satisfactory law of the temperature variation of the resistance.